

AD 747556

FTD-MT-24-1633-71

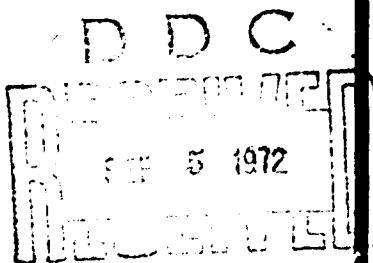
FOREIGN TECHNOLOGY DIVISION



THE REGULARITIES OF THE HIGH-TEMPERATURE
REACTION OF GRAPHITE DURING DIFFUSION OF
THE SOLID PHASE

by

Ye. S. Golovina, L. L. Kotova



Approved for public release;
distribution unlimited.

Reproduced by
**NATIONAL TECHNICAL
INFORMATION SERVICE**
U S Department of Commerce
Springfield VA 22151

18

UNCLASSIFIED

Security Classification

DOCUMENT CONTROL DATA - R & D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY (Corporate author) Foreign Technology Division Air Force Systems Command U. S. Air Force	2a. REPORT SECURITY CLASSIFICATION UNCLASSIFIED
3. REPORT TITLE THE REGULARITIES OF THE HIGH-TEMPERATURE REACTION OF GRAPHITE DURING DIFFUSION OF THE SOLID PHASE	2b. GROUP

4. DESCRIPTIVE NOTES (Type of report and inclusive dates)

Translation

5. AUTHOR(S) (First name, middle initial, last name)

Ye. S. Golovina, L. L. Kotova

6. REPORT DATE 19 Nov 1965	7a. TOTAL NO. OF PAGES 12	7b. NO. OF REFS 2
8a. CONTRACT OR GRANT NO.	8b. ORIGINATOR'S REPORT NUMBER(S) FTD-MT-24-1633-71	
9. PROJECT NO.	10. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)	
d. DIA TASK T71-04-03		

10. DISTRIBUTION STATEMENT

Approved for public release; distribution unlimited.

11. SUPPLEMENTARY NOTES	12. SPONSORING MILITARY ACTIVITY Foreign Technology Division Wright-Patterson AFB, Ohio
-------------------------	---

13. ABSTRACT

Experimental investigation of the interaction between graphite and carbon dioxide at high temperatures (up to 3200 K), when the interaction process is in its limiting diffusion state. It is found that at temperatures higher than 2500 K, the interaction process is accompanied by diffusion of carbon from the bulk to the reacting surface of a sample. Diffusion of graphite is analyzed (analythically) for conditions of one dimensional unsteady diffusion. The self diffusion coefficient of carbon is determined, together with its temperature dependence for temperatures between 2800 and 330 K. Gosudarstvennyi Nauchno-Issledovatel'skii Energeticheskii Institut, Moscow, USSR AT0143082

Security Classification

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
High Temperature Effect Graphite Carbon Dioxide Temperature Dependence Diffusion Coefficient Combustion Conference						

ii

UNCLASSIFIED

Security Classification

FTD-MT- 24-1633-71

EDITED MACHINE TRANSLATION

FTD-MT-24-1633-71

THE REGULARITIES OF THE HIGH-TEMPERATURE REACTION
OF GRAPHITE DURING DIFFUSION OF THE SOLID PHASE

By: Ye. S. Golovina, L. L. Kotova

English pages: 12

Source: Vsesoyuznoy konferentsii po goreniiyu
tverdogo topliva. 2nd 19-23 November
1965. Trudy, (II All-Union Conference
on the Combustion of Solid Fuel, 19-23
November 1965, Izd Vo Nauka, Novosibirsk
1969, pp. 107-113.

Requester: FTD/PDT

This document is a SYSTRAN machine aided
translation, post-edited for technical
accuracy by: Charles T. Ostertag Jr.

Approved for public release;
distribution unlimited.

THIS TRANSLATION IS A RENDITION OF THE ORIGINAL
FOREIGN TEXT WITHOUT ANY ANALYTICAL OR
EDITORIAL COMMENT. STATEMENTS OR THEORIES
ADVOCATED OR IMPLIED ARE THOSE OF THE SOURCE
AND DO NOT NECESSARILY REFLECT THE POSITION
OR OPINION OF THE FOREIGN TECHNOLOGY DIVISION.

PREPARED BY:

TRANSLATION DIVISION
FOREIGN TECHNOLOGY DIVISION
WP-AFB, OHIO.

FTD-MT- 24-1633-71

Date 19 May 1972

U. S. BOARD ON GEOGRAPHIC NAMES TRANSLITERATION SYSTEM

Block	Italic	Transliteration	Block	Italic	Transliteration
А а	А а	А, a	Р р	Р р	Р, r
Б б	Б б	Б, b	С с	С с	С, s
В в	В в	В, v	Т т	Т т	Т, t
Г г	Г г	Г, g	У у	У у	У, u
Д д	Д д	Д, d	Ф ф	Ф ф	Ф, f
Е е	Е е	Ye, ye; Е, e*	Х х	Х х	Х, kh
Ж ж	Ж ж	Zh, zh	Ц ц	Ц ц	Ts, ts
З з	З з	Z, z	Ч ч	Ч ч	Ch, ch
И и	И и	I, i	Ш ш	Ш ш	Sh, sh
Я я	Я я	Y, y	Щ щ	Щ щ	Shch, shch
К к	К к	K, k	Ь ъ	Ь ъ	"
Л л	Л л	L, l	Ы ы	Ы ы	Y, y
М м	М м	M, m	Ь ь	Ь ь	"
Н н	Н н	N, n	Э э	Э э	E, e
О о	О о	O, o	Ю ю	Ю ю	Yu, yu
П п	П п	P, p	Я я	Я я	Ya, ya

* ye initially, after vowels, and after т, б; е elsewhere.
 When written а; ё in Russian, transliterate as yе or ё.
 The use of diacritical marks is preferred, but such marks
 may be omitted when expediency dictates.

FOLLOWING ARE THE CORRESPONDING RUSSIAN AND ENGLISH
 DESIGNATIONS OF THE TRIGONOMETRIC FUNCTIONS.

Russian	English
sin	sin
cos	cos
tg	tan
ctg	cot
sec	sec
cosec	csc
sh	sinh
ch	cosh
th	tanh
cth	coth
sch	sech
csch	csech
arc sin	sin ⁻¹
arc cos	cos ⁻¹
arc tg	tan ⁻¹
arc ctg	cot ⁻¹
arc sec	sec ⁻¹
arc cosec	csc ⁻¹
arc sh	sinh ⁻¹
arc ch	cosh ⁻¹
arc th	tanh ⁻¹
arc cth	coth ⁻¹
arc sch	sech ⁻¹
arc csch	csech ⁻¹
rot	curl
lg	log

THE REGULARITIES OF THE HIGH-TEMPERATURE REACTION OF GRAPHITE DURING DIFFUSION OF THE SOLID PHASE

Ye. S. Golovina, L. L. Kotova

(Power Institute im. G. M. Krzhizhanovskogo)

Experimental investigation of the interaction of graphite with gases until recently was conducted at temperatures not higher than 1800-2000°C. Only in recent time the temperature range of investigation was expanded. As a rule the conditions of experiment in this case correspond to the interaction of graphite with gases in the diffusion area of reaction. Hence it is considered that the entire process is developed at the gas-solid body boundary, only the behavior of the gas phase is considered, and the solid phase remains constant in volume.

However, the expansion of the temperature range of investigations up to 3300°K made it possible to reveal some features of the interaction of graphite with gases and forces us to change our point of view somewhat. Thus during the interaction of carbon with carbonic acid and oxygen [1-3] in the temperature ranges above 2000°C (when the conditions of the developed diffusion mode of reaction will be realized and the possibility of the penetration of the gas phase inside the reacting specimen is eliminated) a change is observed in the density of the solid

body with the preservation or comparatively small change in the dimension of the sample. Qualitatively the established picture is analogous to that which has to be observed for a reaction in the range of the lowest temperatures, when there is the diffusion penetration of gas into the volume of sample and its reaction in bulk [4]. However, in this case the process as a whole is found in its maximum diffusion state, but at the same time the expenditure of solid phase from the internal parts of body occurs.

The discovered phenomenon of the decrease in density in the bulk of the reacting solid body characterizes the unique new high-temperature mode of "internal reacting."

For the purpose of studying the basic regularities of this phenomenon and clarification of its nature a cycle of experiments was conducted in which primarily the density distribution of carbon in the volume of the reacting object was determined with a variation of various parameters, primarily time and temperature.

The work was conducted with spherical carbon particles with a diameter of 15 mm made from graphitized [VTM-4] = (GTM-4) carbon at the Kudinovsk plant. The carbon particle was heated in the inductor of a high-frequency generator. The interaction rate was determined by the method of suspension. Furthermore the change in the diameter of the sample with time was photographically fixed. The particle was photographed in two aspects - frontal and lateral. The treatment of the film and the measurement of the dimensions of particles before and after the experiment were conducted with the [IT] = (IT) instrument microscope which allows the measuring of diameter with an accuracy of ± 0.005 mm.

The temperature was measured with a photoelectric pyrometer. The depth of disintegration of carbon and the density distribution (concentration) of carbon along the radius of the sample

were evaluated by means of the series removal from the sample of layers of carbon 0.2-0.25 mm thick and the determination of the density of the removed layer. For this purpose the spherical particles were passed in series through metallic diaphragms, the diameters of which differed by 0.5 mm. The layers were removed until the nuclear density of the particle was equal to initial. Basic data were obtained in the example of the interaction of carbon with carbon dioxide. The relative concentration of carbon dioxide was 50% with diluent nitrogen; the velocity of flow was equivalent to 0.6 m/s. A small share of the experiments were conducted with oxygen. For the comparative evaluation of the nature of change in density it was more convenient to use not time, but the degree of removal of carbon (gasification) from the sample.

The general picture which characterizes the participation of the internal areas of the carbon sample in reacting in wide temperature range of 1400-3300°K is represented in Fig. 1. This figure depicts the simultaneous change in the depth of disintegration of the sample h_{cm} and the relatively change in the dimensions of the spherical particle d/d_0 for the time of the experiment which corresponds to different degrees of removal from 3 to 29%.

In the area of comparatively low temperatures - 1400-1600°K - a gradual and small decrease in the depth of disintegration with an increase of temperature is noticeable with the simultaneous insignificant reduction in diameter. Further, up to 2500°K the depth remains constant with a substantial change in the diameter of the particle and does not depend on the degree of removal, i.e., time of reacting.

The results presented indicate the quasi-stationary state of the reaction zone at temperatures of 1600-2500°K. The reaction zone of constant depth is shifted on the radius with a

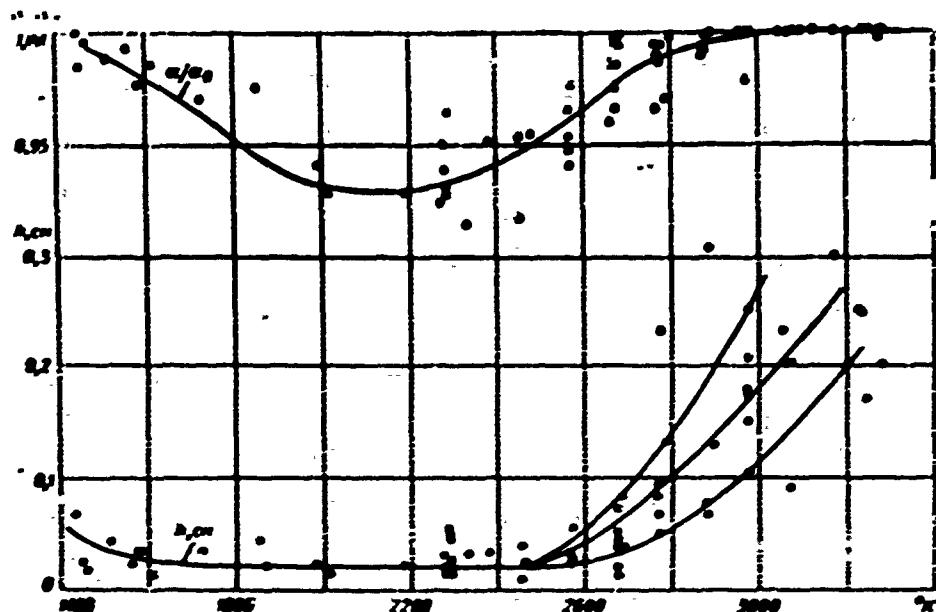


Fig. 1. The change in the depth of penetration of the reaction and relative change in the diameter of the sample depending on temperature: ● - 3-5%; ○ - 15-20%; ■ - 20-30%.

change in the dimensions of the reacting sample. The depth of the zone is small, it comprises 0.2 mm. Actually this indicates that the reaction flows on the surface, which in turn testifies to realization at these temperatures of the maximum diffusion zone of the process of the interaction of carbon with carbon dioxide. The rate of the process in this case determines the magnitude of diffusion flow of the gas phase to the surface.

The further temperature increase leads to an increase in the depth of disintegration with a simultaneous increase in the relative diameter of the particle, which for a temperature of more than 2900°K becomes practically constant and equal to initial. Furthermore it turned out that for $t > 2500^{\circ}\text{K}$ the depth of disintegration depends strongly on the time of reacting. In this case, as it was shown, the applied gas flow is expended on the surface at lower temperatures, all the more according to all data it should be expended on the surface at elevated temperatures.

Figure 2 depicts the picture of the density distribution of carbon on the radius of a spherical particle and its transformation with a change of temperature and time of removal. In Fig. 2a - for temperatures of 2280-2970°K (the degree of removal - 18.5%) and 3070-3270°K (the degree of removal - 10%); in Fig. 2b - for one temperature (2770°K), but different degrees of removal (from 18 to 29%), which answers to the time range 150-300 s. Analogous experimental material has been obtained for various degrees of removal of carbon at various temperatures.

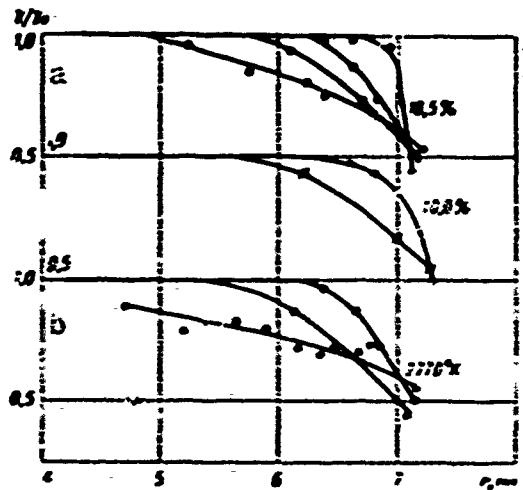


Fig. 2. The density distribution of carbon on the radius of a spherical particle for different temperatures and degrees of removal. a - temperature (°K): \circ - 2280; \bullet - 2770; \square - 2890; \bullet - 2970; \circ - 3070; \blacksquare - 3270°K; b - the degree of removal (%): \circ - 18.5; \circ - 25; \bullet - 29.

It is evident from the figures that in proportion to the temperature increase and increase in the reaction time carbon will be carried out from increasingly deeper layers of the sample, i.e., a particularly nonstationary process is present. Further the nature of the density distribution is analogous to the distribution of concentration during the diffusion of a substance from a solid body [5]. One should also focus attention on the fact that the value of relative surface density for a wide range of temperature and degrees of removal (15-29%) proves to be not so different and fluctuates around a value close to 0.5.

The change of this value from the degree of removal in the example of a reaction at 2770°K is shown in Fig. 4, from which it follows that the constant value of surface concentration is established for the degree of removal more than 15%, which answers to a time of more than 150 s. In Fig. 3 the value of relative surface density γ_s/γ_0 is presented for a wide range of temperature and degrees of removal of 15-30%. It is also close to a value of 0.5. At highest temperature (3000°K), where the obtaining of laboratory findings for long times and respectively greater degrees of removal is complex, results have been obtained for a degree of removal of 8-10%. However, because of the high degree of intensity of the process of the interaction and transfer of carbon the process comes to an established state for a degree of removal of 8-10%, which is testified to especially by the fact that the relative surface density reaches a value of 0.5, characteristic for the steady state process.

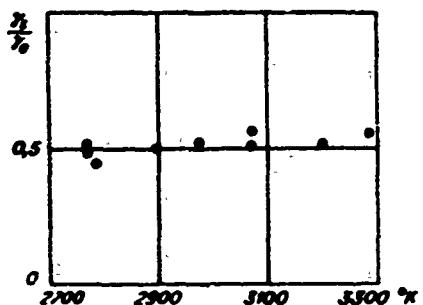


Fig. 3.

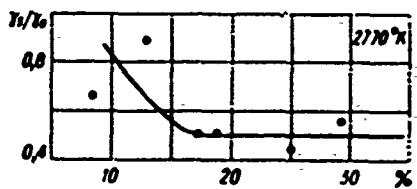


Fig. 4.

Fig. 3. The dependence of relative magnitude of surface density on temperature for the degrees of removal 15-30%.

Fig. 4. The dependence of relative magnitude of surface density on the degree of removal of carbon for $T = 2770^{\circ}\text{K}$.

Keeping in mind the experimental fact that the depth of disintegration as compared with the radius of the particle is small and the fact that the nature of the density distribution in samples for various temperatures and times of removal (under the condition when the dimensions of particles remain practically

constant) is identical with the known distribution of concentration in the case of nonstationary diffusion from a semi-bounded space, we can for the analysis of experimental material include this problem under the following boundary conditions:

$$\text{for } t = 0 \text{ and } -\infty < x < 0 \quad \gamma = \gamma_0 = \text{const};$$

$$\text{for all } t > 0 \text{ and } x = 0 \quad \gamma = \gamma_s = \gamma_0/2,$$

where γ_s - density at the phase boundary.

For such conditions the solution of Fick's second equation for one-dimensional nonstationary diffusion

$$\frac{\partial \gamma}{\partial t} = D_c \frac{\partial^2 \gamma}{\partial x^2},$$

when the diffusion constant does not depend on concentration and is expressed through the known error function of Gauss [6], i.e.

$$\gamma = \frac{\gamma_0}{2} \left\{ 1 + \Phi \left(\frac{x}{2\sqrt{D_c t}} \right) \right\}, \quad (1)$$

where

$$\Phi \left(\frac{x}{2\sqrt{D_c t}} \right) = \frac{2}{\sqrt{\pi}} \int_0^{\frac{x}{2\sqrt{D_c t}}} e^{-\xi^2} d\xi, \quad (2)$$

and x in our case $R - r$.

The integral for the distribution function of Gauss errors is calculated simply according to the mathematical tables which are given in various manuals [6, 7].

Using correlation (1) based on the values γ/γ_0 obtained

from the experiment it is easy to calculate the coefficient of self-diffusion of carbon. The evaluation of the coefficient of self-diffusion for the nonstationary conditions of our problem is permissible when after a sufficient time from the beginning of the process a routine mode is established [5]. A distinctive feature of the routine mode is the linear dependence between the logarithm of concentration and time [8]. From the laboratory findings presented in Fig. 5 it follows that such a routine mode for a temperature of 2770°K is established when removal exceeds 15%, which answers to a time of more than 150 s from the beginning of the process. At such times a constancy of γ_S and equality of $\gamma_S/\gamma_0 = 0.5$ are attained.

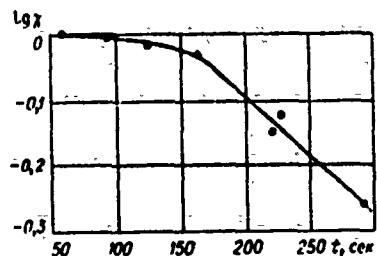


Fig. 5. The density change of carbon from the time of the interaction of carbon with gas for $T = 2770^{\circ}\text{K}$.
Designation: $\text{cek} = s$.

For higher temperatures, when the process flows more intensely, the routine mode will be established more rapidly, which is testified to in particular by the fact that $\gamma_S/\gamma_0 = 0.5$ for these temperatures already at 8-10% of removal.

The values calculated from correlation (1) for the coefficient of self-diffusion of carbon D_C are presented in the following Fig. 6 and in Table 1.

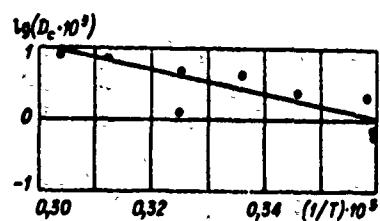


Fig. 6. Change of $\lg(D_C \cdot 10^5)$ from $1/T \cdot 10^3$.

Table 1.

T, °K	$D_C \cdot 10^8 \text{ cm}^2/\text{sec}$	T, °K	$D_C \cdot 10^8 \text{ cm}^2/\text{sec}$
2770	0,70	3070	1,19
2770	0,62	3070	4,54
2780	2,00	3200	6,78
2890	2,24	3280	8,00
2970	4,23		

Designation: $\text{cm}^2/\text{sec} = \text{s.}$

Between $\lg [D_C \cdot 10^5]$ and $1/T \cdot 10^3$ a linear dependence is established, and this witnesses to the fact that the coefficient of self-diffusion of carbon is connected with temperature by the correlation

$$D_C = D_{CO} e^{-\frac{E}{RT}}.$$

In this case $E = 55,000$ calories per mole, and $D_{CO} = 0.5$. The exponential dependence of D_C on temperature and the great significance of activation energy are characteristic for diffusion processes in a solid body.

The correlation obtained for the coefficient of self-diffusion apparently gives a value for D_C which is suitable for estimated calculations. Further works in this direction make it possible to refine this value.

Figure 7 depicts the laboratory findings for the relative density of γ/γ_0 depending on the criterion $Z = R - r/2\sqrt{D_C t}$. The experimental points which correspond to various temperatures, radii, and to the times of the experiments are grouped around one curve. From this it is evident that for $t > 2700^\circ\text{K}$, when the process of the diffusion of carbonic atoms occurs quite intensely and initial dimensions are hardly changed, the distribution of the concentration of solid phase is adequately described by the problem of nonstationary diffusion of a solid phase from

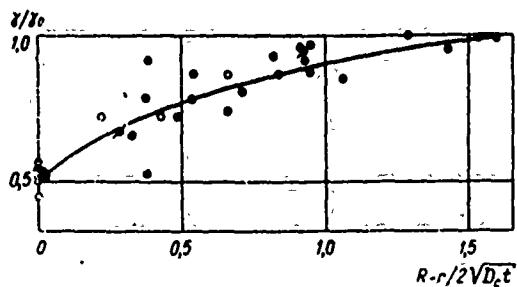


Fig. 7. Dependence of γ/γ_0 on the criterion $\frac{R-r}{2\sqrt{D_c t}}$. Temperature (°K): ● - 2770; ○ - 2780; ● - 2890; ○ - 2970; ● - 3070; ○ - 3200; ■ - 3280.

semi-bounded space.

Thus the physical picture of the phenomenon discovered is represented in the following manner.

Under the conditions of a high-temperature developed diffusion mode of reaction the applied flow, as it was shown, is expended on the surface.

In the surface layer of a solid body due to the reaction of carbon atoms with structural imperfections, point vacancies are formed. High temperatures ensure the significant mobility of the atoms of carbon in the crystal lattice [9, 10]. Only in an ideal crystal lattice, which under all conditions preserves an ideal order, there cannot be any diffusion of atoms.

An ideal crystal does not possess a correct structure, and carbon as a polycrystalline body - all the more. In such a crystal lattice due to breakdowns the movements of atoms, their diffusion, can arise. The atoms will strive to occupy the freed places (vacancies) in lattice at the surface, and vacancies themselves will move in their place and will determine the decrease in density in its volume.

Furthermore the endothermic reaction on the surface of the sample and the cold incident flow of the active gas will determine the existence of the temperature gradient on radius of a

particle. Therefore the flow of carbon atoms from the volume of body to its surface develops. In this case a significant density change will be observed and simultaneously the small or complete absence of the change in the dimensions of the sample.

It is natural in the area of lower temperatures the diffusion of carbon takes place thusly, however, it is relatively small. Feldman [10], using the method of labelled atoms, observed the self-diffusion of carbon at comparatively low temperatures of 2100-2600°K. The laboratory findings obtained by him did not make it possible to evaluate directly the activation energy of the self-diffusion of carbon. Only by including the theoretical results of Dienes [11], M. N. Feldman obtained a value of activation energy equal to 75,000 calories/per mole.

It follows from the given point of view that the density change of carbon at elevated temperatures should be exhibited during its reaction with any reagent because any reaction will create defects in the lattice. The conditions of the experiment — the velocity of flow, the concentration of gas reagent and its nature — will determine the surface concentration of vacancies and the flow value of carbon atoms from the volume in the range of temperatures where the diffusion of carbon atoms is great and the characteristics of the transfer of gas reagent and flow of carbon are commensurable.

In conclusion it is necessary to note that during the study of the interaction of graphite with gas up to now the proper value was not attached to the structural defects of graphite and to their influence on the flow of this process. Experimental material was considered as relating to material which was ideal in a crystallographic respect. The presence of an internal diffusion process of the transfer of the solid substance itself during its reaction in a chemically active gaseous environment specified by the existence of defects, forces us to reexamine

the existing point of view on the behavior of the reacting solid body. In general in the analytical examination of problem about its reaction one must take into account the behavior not only of the gas phase, but also the substance of the solid body. For many problems precisely the behavior of the most reacting solid substance is of interest, and only in such an examination will it be possible to obtain information about the change in the porosity or apparent specific weight of a sample.

BIBLIOGRAPHY

1. On the basis of the laboratory findings on the interaction of graphite with carbon dioxide at high temperatures — up to 3200°K — it was established that at temperatures greater than 2500°K the process of the diffusion carrying out of carbon from the volume of a solid body to the reacting surface begins to be exhibited. The regularities of this process have been studied experimentally.
2. An analytical analysis is made of the process of the diffusion of graphite for the conditions of one-dimensional nonstationary diffusion. The coefficient of self-diffusion of carbon and its temperature dependence for the range $2800-3300^{\circ}\text{K}$ have been determined.